

# Production of hydrogen peroxide from oxygen and alcohols, catalyzed by palladium complexes

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## Abstract

Production of hydrogen peroxide has been achieved by the catalytic oxidation of primary and secondary alcohols with oxygen, in presence of a palladium catalyst. The catalyst was a complex of palladium with a bidentate nitrogen ligand and an acid cocatalyst. 2,9-Dimethyl-4,7-diphenyl-1,10-phenantroline (**1**) was selected as the most efficient ligand, and perfluorooctanoic acid gave the best results as cocatalyst. In this work the effects of nitrogen ligands, acid cocatalyst, alcohols, as far as temperature and oxygen pressure are concerned, are investigated. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Hydrogen peroxide; Alcohol oxidation; Palladium; N-ligands

## 1. Introduction

The tendency of alcohols to reduce Pd(II) species was already described in 1828 by Berzelius, who reported the reduction of most of the Pd from a wet ethanolic solution of  $K_2PdCl_4$  [1].

In 1977, Schwartz carried out a catalytic oxidation of alcohols using oxygen as reoxidant of Pd [2]. Many other studies about the catalytic oxidation of alcohols with palladium have been reported, mainly concerning palladium salts, under basic conditions [3–5]. Catalysis by salts

[6,7], complexes [8] or Pd clusters [9,10] in the absence of base have also been described.

In all the cases, and to the best of our knowledge, the only compounds obtained by the reaction were the alcohol oxidation products and water.

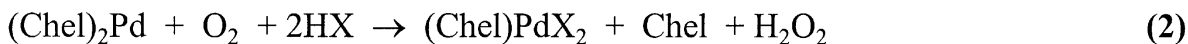
As a part of an industrial research aimed to the direct synthesis of hydrogen peroxide from water, oxygen and carbon monoxide, in presence of a palladium complex with nitrogen ligands, we found that alcohols can act themselves as reducing agents of the palladium complexes, instead of carbon monoxide, with production of hydrogen peroxide and of the corresponding carboxylic compounds.

The process is illustrated in Scheme 1.

Chel is a bidentate nitrogen ligand and X is the anion of an acid cocatalyst. The same catalytic system,  $(Chel)PdX_2$ , was effective in the

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Scheme 1.

direct synthesis of hydrogen peroxide from water and oxygen, using carbon monoxide as reducing agent, previously reported by our group [11].

The carbonylic compound produced with hydrogen peroxide can turn out advantageous if an economically interesting product is obtained, for example cyclohexanone, that is an intermediate of the caprolactam synthesis.

Although the reaction (3) is formally similar to the alcohol autooxidation [12], the mechanism is in substance different. It is proved by the fact that, contrary to the alcohol autooxidation, this reaction occurs on a wide variety of primary and secondary alcohols and only in presence of the catalyst. Besides, it can be carried out at a temperature notably lower than that necessary for the alcohol autooxidation (70°C instead of 130°C).

## 2. Experimental

The ligands used in this study were: 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (2,9-dm-4,7-dpphen) (1), 2,9-dimethyl-1,10-phenanthroline (2,9-dmphen) (2), 4,7-diphenyl-1,10-phenanthroline (4,7-dpphen) (3), 1,10-phenanthroline (phen) (4), 2,9-*n*-dibutyl-1,10-phenanthroline (2,9-dbphen) (5), 2,9-diphenyl-1,10-phenanthroline (2,9-dpphen) (6), and 2,4,6-tripyridyl-triazine (tpytaz) (7). Ligands 1–4 and 7 were purchased from Aldrich.

Ligands 5 and 6 were synthesized according to the procedures described in the literature [13,14].

### 2.1. General procedure for the synthesis of hydrogen peroxide

11.2 mg (0.05 mmol) of palladium acetate and 36 mg (0.1 mmol) of 2,9-dm-4,7-dpphen were dissolved in 5 ml of chlorobenzene and stirred for 6 h at 25°C.

0.5 ml of this solution (corresponding to 0.005 mmol Pd and 0.01 mmol ligand) are added to 4.5 ml of cyclohexanol and 25 mg (0.06 mmol) of C<sub>7</sub>F<sub>15</sub>COOH and stirred 1 h at 60°C. The resulting solution was added to 5 ml of water to form a biphasic system and poured into an autoclave containing a glass liner. The reactor was then pressurized to 5 atm pressure of O<sub>2</sub>. The reaction was carried out for 1 h at 70°C, with the mixture being stirred by a magnetically driven impeller. After depressuring the reactor, the hydrogen peroxide concentration in the aqueous solution was measured by titration with potassium permanganate, while the carbonylic compound content was determined by gaschromatographic analysis.

The described procedure can be applied to all the ligands 1–7.

## 3. Results and discussion

The reaction was carried out in a biphasic system, consisting of water and a water-immiscible alcohol. The catalyst was a complex of

Table 1

Nitrogen ligand effect

Catalyst: Pd(OAc)<sub>2</sub>; acid cocatalyst: C<sub>7</sub>F<sub>15</sub>COOH; T = 70°C; pO<sub>2</sub> = 5 atm; [Pd] = 5 · 10<sup>-3</sup> mmol.

Ligand	Alcohol	TOF <sup>a</sup>
2,9-dm-4,7-dpphen ( <b>1</b> )	cyclohexanol	221
2,9-dmpphen ( <b>2</b> )	cyclohexanol	115
4,7-dpphen ( <b>3</b> )	cyclohexanol	0
phen ( <b>4</b> )	cyclohexanol	0
2,9-dbphen ( <b>5</b> )	cyclohexanol	0
2,9-dpphen ( <b>6</b> )	cyclohexanol	0
2,4,6-tpytaz ( <b>7</b> )	cyclohexanol	66

<sup>a</sup>Turnover number frequency (calculated as mole of hydrogen peroxide per moles of palladium per hour).

palladium with nitrogen ligands, soluble in the organic phase, in presence of an acid as cocatalyst.

The biphasic system minimizes the ligand oxidation by reducing its contact with hydrogen peroxide and enables the separation and recycling of the catalyst by simple decantation.

The catalyst was generated in situ from palladium acetate, 2 equivalents of one of the ligands **1–7** and 12 equivalents of the acid cocatalyst.

Table 1 shows the ligand effect on the complex catalytic activity, with cyclohexanol used both as solvent and reducing agent. As already found for the synthesis of hydrogen peroxide from oxygen and carbon monoxide, also in this case we observed a different behaviour depending on the nature of the substitution in 2,9-position of the ligand.

Table 2

Effect of the acid cocatalyst

Catalyst: Pd(OAc)<sub>2</sub>; T = 70°C; pO<sub>2</sub> = 5 atm; [Pd] = 5 · 10<sup>-3</sup> mmol.

Ligand	Acid cocatalyst	Alcohol	TOF <sup>a</sup>
<b>1</b>	C <sub>7</sub> F <sub>15</sub> COOH	cyclohexanol	221
<b>1</b>	CF <sub>3</sub> COOH	cyclohexanol	148
<b>1</b>	HCl	cyclohexanol	49
<b>1</b>	CH <sub>3</sub> COOH	cyclohexanol	76
<b>1</b>	H <sub>2</sub> SO <sub>4</sub>	cyclohexanol	78
<b>1</b>	H <sub>3</sub> PO <sub>4</sub>	cyclohexanol	91

<sup>a</sup>Turnover number frequency (calculated as mole of hydrogen peroxide per moles of palladium per hour).

TOF

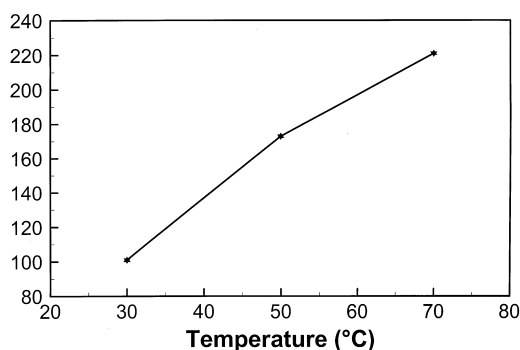


Fig. 1. Effect of the temperature. Catalyst: Pd(OAc)<sub>2</sub>; ligand 2,9-dm-4,7-dpphen; acid cocatalyst: C<sub>7</sub>F<sub>15</sub>COOH; pO<sub>2</sub> = 5 atm; alcohol:cyclohexanol; [Pd] = 5 · 10<sup>-3</sup> mmol. TOF = turnover number frequency (calculated as mole of hydrogen peroxide per moles of palladium per hour).

Only 2,9-substituted phenanthrolines (**1**, **2**) and 2,4,6-trisubstituted triazine (2,4,6-tpytaz) (**7**) were effective in the alcohol oxidation and H<sub>2</sub>O<sub>2</sub> production. In particular, the best results were obtained with 2,9-dm-4,7-dpphen (**1**) which showed the optimum steric and electron-donating capacity for the palladium activation.

2,9-dmpphen (**2**) gave a water soluble complex which became active only if carried in the organic phase by using the hydrophobic cocatalyst C<sub>7</sub>H<sub>15</sub>COOH, acting as phase transfer anion

TOF

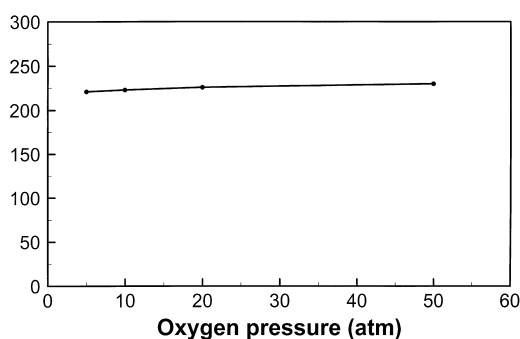


Fig. 2. Effect of the oxygen pressure. Catalyst: Pd(OAc)<sub>2</sub>; ligand 2,9-dm-4,7-dpphen; acid cocatalyst: C<sub>7</sub>F<sub>15</sub>COOH; T = 70°C; alcohol:cyclohexanol [Pd] = 5 · 10<sup>-3</sup> mmol. TOF = turnover number frequency (calculated as mole of hydrogen peroxide per moles of palladium per hour).

(the partition of the complex with ligand **2** in the organic layer was < 1% and > 99% with trifluoroacetate and perfluorooctanoate, respectively).

The ligands **5–6**, 2,9-dbphen and 2,9-dpphen, bearing bulky substituents, lead to the formation of unreactive stable complexes, probably due to their steric hindrance adjacent to the N-donor function.

The 2,9-unsubstituted ligands, 4,7-dpphen (**3**) and phen (**4**), were also inactive, even if used with a highly lipophilic acid, probably because of the formation of aggregated species that are ineffective in the given reaction.

As shown in Table 2, using ligand **1**, we tested a series of acid cocatalysts. Fluorinated acids, and in particular perfluorooctanoic acid gave better results than acetic and mineral acids such as sulphuric, phosphoric and hydrochloric acids. It is worth noting that the strongly coordinating chloride ion did not act as inhibitor on the reaction as in the case of the previously described O<sub>2</sub>/CO process.

All reactions were performed at 70°C and 5 atm of oxygen. The temperature was chosen as the best compromise between H<sub>2</sub>O<sub>2</sub> production and H<sub>2</sub>O<sub>2</sub> stability. As shown in Fig. 1, we found a direct proportionality between temperature and catalytic activity. Higher temperatures led to the H<sub>2</sub>O<sub>2</sub> degradation.

Increasing the oxygen pressure did not affect notably the reactivity, leading only a slight improvement of the activity, as reported in Fig. 2.

On the basis of this result, the reaction could be carried out using air instead of oxygen without any catalyst degradation due to the precipitation of reduced palladium.

As reported in Table 3, among a wide variety of primary and secondary alcohols, tested as reducing agents, cyclohexanol gave the higher activity, with a TOF of 221, corresponding to 0.75% (w/w) of hydrogen peroxide in the aqueous phase.

Cyclohexanol and 1-phenylethanol, in the same reaction conditions but in absence of catalyst, did not lead to H<sub>2</sub>O<sub>2</sub> production, confirm-

Table 3

Effect of alcohol

Catalyst: Pd(AcO)<sub>2</sub>; T = 70°C; pO<sub>2</sub> = 5 atm; [Pd] = 5 · 10<sup>-3</sup> mmol.

Ligand	Acid cocatalyst	Alcohol	TOF <sup>a</sup>
– <sup>b</sup>	–	Cyclohexanol	(0)
– <sup>b</sup>	–	1-Phenylethanol	(0)
<b>1</b>	C <sub>7</sub> F <sub>15</sub> COOH	1-Phenylethanol	152
<b>1</b>	C <sub>7</sub> F <sub>15</sub> COOH	1-Phenyl-1-propanol	44
<b>1</b>	C <sub>7</sub> F <sub>15</sub> COOH	1-Phenyl-2-propanol	123
<b>1</b>	C <sub>7</sub> F <sub>15</sub> COOH	Cyclohexanol	221
<b>1</b>	C <sub>7</sub> F <sub>15</sub> COOH	2-Propanol	102
<b>1</b>	C <sub>7</sub> F <sub>15</sub> COOH	2-Octanol	34
<b>1</b>	C <sub>7</sub> F <sub>15</sub> COOH	1-Pentanol	105
<b>1</b>	C <sub>7</sub> F <sub>15</sub> COOH	2-Ethylhexanol	138
<b>1</b>	C <sub>7</sub> F <sub>15</sub> COOH	1-Octanol	134
<b>1</b>	C <sub>7</sub> F <sub>15</sub> COOH	Benzyl alcohol	127
<b>1</b>	C <sub>7</sub> F <sub>15</sub> COOH	4-Methoxybenzyl alcohol	35

<sup>a</sup>Turnover number frequency (calculated as mole of hydrogen peroxide per moles of palladium per hour).

<sup>b</sup>The reaction was carried out without catalyst.

ing that the process does not proceed via auto-oxidation pathway.

Simultaneously to the hydrogen peroxide, an equimolecular amount of ketone is produced, thus excluding the rising up of secondary reactions leading to the consumption of hydrogen peroxide [15].

In conclusion, complexation of palladium with a suitable nitrogen ligand provided an efficient catalyst for the oxidation of alcohols with oxygen and simultaneous synthesis of hydrogen peroxide.

Peculiarly, the reaction proceeds both with primary and secondary alcohols, under mild conditions of temperature and oxygen pressure, confirming that no alcohol autooxidation occurs.

Likewise, the process with CO/O<sub>2</sub> and water, the structure of the ligand as well as the nature of the acid cocatalyst plays a key role in determining the catalytic activity.

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